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On the Direct Reduction of Arsonic Acids to Arsenoso Compounds: Mechanisms and Preparations†

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By using a variety of reducing agents, either alone or in the presence of iodide as a catalyst, the reduction of arsonic acids to arsenoso compounds and/or arsonous acids has been studied. The solvent and temperature are important for a clean reduction. The mechanism of the reduction involves prior protonation of the —AsO_3H_2 group, and can be rationalized in the framework of the 'hard and soft acids and bases' principle, which is used to predict other reducing systems and to explain other literature data. For preparative purposes, triphenylphosphine/iodine, hexamethylphosphorous triamide/iodine and ascorbic acid/iodine give flexibility of choice depending on the substrate. The first two of these systems decompose arsonic acids with a weak C–As bond but the last system is sufficiently mild towards the same arsonic acids.

Keywords: arsonic acids; arsenoso compounds; arsonous acids; ascorbic acid; triphenylphosphine; hexamethylphosphorous triamide

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INTRODUCTION

The chemical reduction of arsonic acids can give various products [arsenoso compounds $(RAsO)_x$ or arsonous acids $RAs(OH)_2$, arseno compounds $(RAs)_x$ or arsines $RAsH_2$], depending on the nature of the arsonic acid (aliphatic or aromatic) and the reducing agent.[1a]

The direct reduction of aliphatic or aromatic arsonic acids to arsenoso compounds has been achieved in a few cases using SO_2/H_2O for $MeAsO_3Na_2$[2,3] and $EtAsO_3H_2$,[4] and $NaHSO_3/H_2O$ or $SO_2/H_2SO_4/H_2O$ for $PhAsO_3H_2$.[4,5] Auger[2] could not reduce $MeAsO_3H_2$ with sulphur dioxide (SO_2) without the presence of I^- as a catalyst.

The preparation of arsenoso compounds is usually effected by reducing the arsonic acid with SO_2 and catalytic amounts of I_2 in concentrated aqueous hydrohalic acid. The co-reductant, SO_2, reduces I_2 to I^- which, in turn, reduces the arsonic acid to the arsenoso compound, being oxidized to I_2. The hydrohalic acid then converts the arsenoso compound to dihaloarsine, which is isolated.[1b,6] Hydrolysis or alkaline hydrolysis of dihaloarsines then produces the arsenoso compounds, but in certain cases this is accompanied by C–As bond rupture.[1b] When the reductant is HI, diiodoarsine, R—AsI_2 is produced either in aqueous or in organic solvents.[7]

Concerning the mechanism of the reduction, Irgolic *et al.*[7] favoured alkyldihydroxydiiodoarsorane, $RAsI_2(OH)_2$, as an intermediate, which loses I_2 to give the arsonous acid.

The reduction of aromatic arsonic acids to arsenoso compounds with phenylhydrazine is not a 'clean' reaction.[1b] Whereas *p*-amino-substituted phenylarsonic acids are reduced by phenylhydrazine to arsenoso compounds,[8] phenylarsonic acid gives triphenylarsine.[9]

Thiols reduce arsonic acids under neutral conditions to give thioarsenites, $RAs(SR')_2$.[10,11] Although thioarsenites are hydrolysed in alkaline solutions,[12,13] they have not been used for the preparation of arsenoso compounds.

Recently, Dixon[14] suggested that boiling 50% aqueous formic acid (HCOOH) can replace the SO_2/H_2O for the iodide-catalysed reduction of arsonic acids to arsenoso compounds. This is an attractive idea because the arsenoso compound can be obtained pure by a simple evaporation.

For the preparation of arsenic, non-isosteric analogues, $RR'AsO_2H$, of naturally occurring phosphate diesters, a mild way to reduce arsonic

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† In memory of my father.

acids to arsenoso compounds, is required. Then, by the Auger reaction,[2] i.e. 'disodium' arsonite and alkyl halide, arsinic acids will be obtained. Herein, we report our studies on the reduction of, mainly, aliphatic arsonic acids to arsenoso compounds by various compounds in the absence and in the presence of a catalyst.

We used as substrates the aliphatic propyl-, allyl-, benzyl- and *rac*-2,3-dihydroxypropylarsonic acids, and the aromatic phenylarsonic acid. Allyl[6] and benzylarsonic[15] acids have a weak C–As bond for they can react with nucleophiles, apart from S_N2, by S_N1 and/or S_N2' (allyl) and S_N1 (benzyl) mechanisms, thus giving arsenic(III) oxide (As_2O_3) which is easily detected either visually or by TLC or IR. Therefore, most of our studies were done with these two arsonic acids because if the reduction is sufficiently gentle for their C–As bond not to be broken, it will be more so for the other arsonic acids, which have a stronger C–As bond.

EXPERIMENTAL

Materials

Triphenyl phosphite was purchased from Merck, and ascorbic acid from Fluka. Trimethyl and triethyl phosphites, phenylarsonic acid, triphenylphosphine, polymer (polystyrene crosslinked with 2% divinylbenzene)-bound triphenylphosphine and hexamethylphosphorous triamide were purchased from Aldrich. Sodium cyanoborohydride (90%) was obtained from Sigma. Allyl-, propyl-, and benzylarsonic acids[16] and *rac*-2,3-dihydroxypropylarsonic acid[11] were prepared by literature methods. The propyl esters of arsonic acids were prepared and used *in situ* according to Dixon.[14] Solvents were analytical grade. Methanol was *not* dried over A_4 molecular sieves. Wet methanol should be used for reductions with ascorbic acid.[17] De-aerated methanol was prepared by boiling, stoppering and cooling to room temperature (RT). The polymer-bound triphenylphosphine was not dried in an oven.[18] Silica gel Si60 (Serva) was used for column chromatography and silica gel H (Merck) for thin-layer chromatography.

Instruments and analyses

Thin-layer chromatography (TLC) was run on microslides, always using appropriate standards. Visualization was effected first by iodine vapour [for Ph_3P, Ph_3PO, $Ph_4P^+Br^-$, propyl-, allyl- and phenylarsonic acids (but not benzylarsonic acid), all arsenoso compounds, and Na_3AsO_3[11,19]], followed by spraying with 35% H_2SO_4 and charring (for ascorbic acid, dehydroascorbic acid, allyl- and benzylarsonic acids). Arsenic(III) oxide was detected by IR[20] and as a solution in aqueous NaOH by TLC and determined titrimetrically in buffered ($NaHCO_3$) solution with standard iodine solution.[21a] IR spectra were obtained on a Perkin-Elmer model 16PC FT-IR spectrometer. ^1H NMR spectra were run on a Bruker DPX Avance (400 MHz) spectrometer. Elemental analyses were done by CNRS, Vernaison, France.

Attempted non-catalysed reductions

Allylarsonic acid

With hydroquinone

Allylarsonic acid (84 mg, 0.5 mmol) and hydroquinone (55 mg, 0.5 mmol) dissolved in de-aerated methanol (1 ml) were stirred at RT for 4 h. TLC (Et_2O/petroleum ether, 3:1) showed only the hydroquinone (R_f 0.61) and no 1,4-benzoquinone (R_f 0.83). No reduction was observed when the solution was acidified with 6 M hydrochloric acid or made alkaline with concentrated ammonia.

With ascorbic acid

Allylarsonic acid (0.5 mmol) and ascorbic acid (0.6 mmol) dissolved in de-aerated methanol (1 ml) were stirred at RT for 3 h. TLC (Et_2O/Me_2CO, 1:1) showed only the ascorbic acid (R_f 0.61) and no dehydroascorbic acid (R_f 0.81).

With triphenylphosphine

Allylarsonic acid (1 mmol) and triphenylphosphine (1 mmol) dissolved in 2 ml methanol/ether (1:1) were stirred at RT for 19 h. TLC (Et_2O/petroleum ether, 3:1) showed only triphenylphosphine ($R_f \approx 1.0$) and no triphenylphosphine oxide (R_f 0.23). No reduction was observed in dimethylformamide (DMF) at 110 °C for 2 h. When the reagents, without solvent, were stirred at 90 °C (oil-bath temperature) for 2 h, the system became brown and consisted mostly of triphenylphosphine with traces of triphenylphosphine oxide.

No reduction was observed when, to the n-propyl ester of allylarsonic acid (prepared by dissolving 2 mmol allylarsonic acid in 3 ml n-propanol, and slowly distilling off the excess n-propanol, leaving a clear colourless oil), a solution of 2 mmol triphenylphosphine in 3 ml toluene was added and

stirred at 100 °C for 3 h. TLC showed unreacted triphenylphosphine and traces of triphenylphosphine oxide.

With triethyl phosphite and triphenyl phosphite
Allylarsonic acid (1 mmol) and triethyl phosphite (1 mmol) were stirred at 95 °C for 4 h. TLC (MeOH/conc. NH_3, 4:1) showed traces of allylarsonic acid. Addition of toluene (1 ml) and centrifugation gave 69 mg of a white solid which by titration was As_2O_3 (64 mg), corresponding to 70% C–As bond fission.

With 100% excess triethyl phosphite, under the same conditions as above, 60% decomposition was found and no odour of the phosphite was perceptible.

Equimolar amounts of allylarsonic acid and triphenyl phosphite in toluene at 85 °C for 3 h gave 67% C–As bond fission.

Benzylarsonic acid

With triethyl phosphite
A suspension of benzylarsonic acid (0.5 mmol) and triethyl phosphite (0.5 mmol) in toluene (1 ml) was stirred at 85 °C for 7 h. After cooling, centrifugation and washing with methanol gave 27 mg arsenic(III) oxide corresponding to 54% C–As bond fission. The supernatant had a bitter-almond (benzaldehyde) smell and TLC (diethyl ether) showed the presence of benzyl alcohol (R_f 0.77).

Phenylarsonic acid

With triethyl phosphite
A suspension of phenylarsonic acid (0.5 mmol) and triethyl phosphite (0.5 mmol) in toluene (1 ml) was stirred at 85 °C for 7 h. The system did not clear. After cooling, centrifugation gave 32 mg of phenylarsonic acid. The supernatant was evaporated, diethyl ether (Et_2O) was added and after 2 days centrifuged. The precipitate (38 mg) was phenylarsonic acid (by TLC and IR).

With sodium cyanoborohydride
Methanol (1 ml) was added to phenylarsonic acid (0.5 mmol) and sodium cyanoborohydride (0.5 mmol), and stirred at RT for 2 h. After an initial evolution of dihydrogen[22] a small amount of a white solid was formed. Centrifugation gave 22 mg of solid which had (by IR) —OH at 3432 cm^{-1}, —CN at 2178 cm^{-1}, As=O at 872 cm^{-1} and —AsO_3H^- at 734 cm^{-1}, pointing to a monoanion of arsonic acids.[23] From the supernatant a solid (99 mg) was obtained which had (by IR) no —OH group, —BH at 2310 cm^{-1},[22] —CN at 2180 cm^{-1}, As=O at 874 cm^{-1}, and —AsO_3H^- at 736 cm^{-1}, thus indicating the presence of $PhAsO_3H^-$.

When methanolic hydrochloric acid (0.5 mmol) was added to phenylarsonic acid (0.5 mmol) in methanol (1 ml), followed by sodium cyanoborohydride, the reaction was exothermic, dihydrogen was evolved and a solid was formed. After 2 h at RT, centrifugation gave 50 mg of a solid which had the same IR spectrum as the white solid mentioned above. The supernatant gave 74 mg of a solid whose IR spectrum was similar to that obtained from the supernatant of the non-acidified reaction.

Attempted iodide-catalysed reductions with aqueous formic acid/iodine

Allylarsonic acid

Allylarsonic acid (83 mg, 0.5 mmol) and 8 mg (6 mol%) iodine dissolved in 1 ml of 50% aqueous formic acid were stirred at 120 °C (oil-bath temperature) for 2 h. A clear colourless solution was obtained after 15 min and arsenic trioxide started precipitating after 90 min. Evaporation, drying and extraction left 16.5 mg As_2O_3 (corresponding to 34% C–As bond fission). From the methanol extracts 49.5 mg of allylarsonic acid were obtained: m.p. 122–124 °C [lit.[16] 128–129 °C]; TLC (MeOH/conc. NH_3, 4:1): R_f 0.62. Thus 94% of the As was recovered.

Benzylarsonic acid

In this case 66% C–As bond fission occurred under the same conditions as above.

Phenylarsonic acid

Of the starting material, 100% was recovered after 7 h at 130 °C in 50% aqueous formic acid and 6 mol% iodine. This was identified by TLC and IR.

Preparative iodide-catalysed reductions with triphenylphosphine/iodine

Phenylarsonic acid

To a mixture of phenylarsonic acid (404 mg, 2 mmol), triphenylphosphine (786 mg, 3 mmol) and iodine (76.2 mg, 0.3 mmol) under nitrogen, de-aerated methanol (2 ml) was added. After 2 h of stirring at RT, a drop of the solution added to three drops of saturated lithium hydroxide in methanol gave no precipitate, indicating that all of the arsonic acid had reacted, and TLC (MeOH, visualization

with I_2 vapour) showed the product as a white/yellowish spot, R_f 0.80; Ph_4P^+ as a purple trailing spot, R_f ≃0.23; and Ph_3P/Ph_3PO, R_f 0.92. After evaporation and drying, the solid dissolved in acetone or chloroform was applied to a column of silica gel (20 g) in acetone. Elution with acetone (200 ml) removed Ph_3P/Ph_3PO and some of the product [probably as $PhAs(OH)_2$] and elution with methanol (150 ml) gave the product (300 mg) as a glass. This was taken up in chloroform (4 ml), leaving behind traces of silica-gel fines (by IR[20]). Evaporation and trituration with diethyl ether gave 292 mg (87%) of the product as a white solid (contaminated by traces of a salt of Ph_4P^+): m.p. 118–120 °C [lit.[5] 118–120, 129–130, 142–145 °C for oligomeric, and 210–220 °C for polymeric arsenosobenzene]. The product was soluble in CH_2Cl_2, $CHCl_3$ or DMF, moderately soluble in MeOH, and insoluble in H_2O, Et_2O, Me_2CO or MeCN. IR (KBr) (cm^{-1}): 1478 w, 1432 m, 1304 w, 1158 w, 1080 m, 1024 vw, 998 vw, 914 w, 742 vs (sh), 722 vs, 692 s, 680 m (sh), 548 m, 520 m.

rac-2,3-Dihydroxypropylarsonic acid

To the impure[11] arsonic acid (200 mg, 1 mmol), dissolved by warming in methanol (2 ml) and cooling to 0 °C under nitrogen, triphenylphosphine (393 mg, 1.5 mmol) and iodine (26 mg, 0.1 mmol) were added and stirred at 0 °C for 2 h. The lithium hydroxide test showed no arsonic acid present and TLC (MeOH) showed the presence of product, (Ph_3P/Ph_3PO) and traces of a salt of $Ph_3P^+CH_2CH(OH)CH_2OH$. Concentration and column chromatography on silica gel (10 g) as above gave, in the methanolic fraction, the product (145 mg) as a glass, which was freed from most of the silica-gel fines by take-up in the methanol (2 ml). The product (141 mg, 85%) was slightly impure because of a salt of $Ph_3P^+CH_2CH(OH)CH_2OH$ (by TLC and NMR), methanol (by NMR) and probably by silica-gel fines. It was very hygroscopic and melted at *ca* 77 °C. The impurities do not interfere with the Auger reaction. IR (KBr) (cm^{-1}): 3380 vs, 2928 m, 2868 m, 1648 m, 1398 m, 1324 m, 1232 m, 1136 s, 1064 s, 1002 s, 945 s, 848 m, 724 s, 626 s, 546 s. ^{1}H NMR (DMSO-d_6) major peaks, δ: 1.15 (s, 0.12H, ?); 1.72 (s), 1.73 (s), 1.75 (s), 1.76 (s), 2.12 (s) and 2.15 (s) for C*H*$_2$As; 3.84 (s), 3.85 (s), 3.87 (s); 3.88 (s) and 4.44 (s) for C*H*$_2$OH; 4.07 (s) and 4.08 (s) for C*H*OH; 4.70, 5.10, 6.51 and 7.30 (broad singlets for C—O*H* and As—O*H*). ^{1}H NMR (D_2O) major peaks, δ: 1.20 (s, ?); 1.90 (s), 1.91 (s), 1.93 (s), 1.95 (s), 2.18 (s) and 2.22 (s) for C*H*$_2$As; 3.88 (s), 3.885 (s), 3.90 (s), 3.91 (s) and 4.54 (s) for C*H*$_2$OH; 4.14 (s) and 4.16 (s) for C*H*—OH.

Preparative iodide-catalysed reduction with polymer-bound triphenylphosphine/iodine

Phenylarsonic acid

The resin (0.1833 g, containing 0.55 mmol phosphorus), suspended in 2 ml DMF, was stirred at RT for 3 h. The DMF was pipetted off, then 2 ml DMF was added followed by 80.8 mg (0.4 mmol) phenylarsonic acid and 4 mg iodine. After stirring at RT for 24 h, centrifugation, washing with 1 ml DMF and evaporation of the DMF (35 °C, 1 mmHg) gave 71 mg of a yellowish film. This was extracted in 1 ml $CHCl_3$, then evaporated to a yellow oil which, after trituration with 1 ml Et_2O, gave 46 mg (70%) of the product as a yellowish solid: m.p. 117–120 °C.

When non-prewashed resin was used, a mixture of arsenosobenzene and Ph_3PO (by IR) was obtained, indicating that 16 mol% of the triphenylphosphine was not bound to the resin.

Allylarsonic acid

After two days of stirring of prewashed resin with allylarsonic acid and 3 mol% iodine in DMF, 81% allylarsonic acid (by TLC and IR) was recovered.

Preparative iodide-catalysed reductions with ascorbic acid/iodine

Phenylarsonic acid

To a colourless solution of phenylarsonic acid (404 mg, 2 mmol) and ascorbic acid (528 mg, 3 mmol) in 2 ml de-aerated methanol, 25 mg (0.1 mmol) iodine was added and the yellowish solution was stirred at RT for 2 h. TLC (Et_2O/Me_2CO, 1:1) showed the dehydroascorbic acid (R_f 0.80) and unreacted ascorbic acid (R_f 0.70) and the lithium hydroxide test showed no arsonic acid to be present. Evaporation and drying gave a yellowish semi-solid.

Isolation by water extraction

The semi-solid was dissolved in chloroform (12 ml) and extracted with water (4 × 8 ml). The chloroform phase was dried (Na_2SO_4), filtered, evaporated and dried to give the pure product (268 mg, 80%), m.p. 128–129 °C.

Isolation by column chromatography

The semi-solid, from a 2 mmol-scale reduction, disssolved in acetone was applied onto a column of

silica gel (20 g) in acetone. Elution with acetone (150 ml) removed the ascorbic and dehydroascorbic acids, and methanol (100 ml) gave the product contaminated with traces of ascorbic acid and silica-gel fines. The latter (38 mg) were removed by adding 3 ml chloroform and centrifuging. From the supernatant, 302 mg (90%) of pure product was obtained as an off-white powder, m.p. 118–119 °C.

Propylarsonic acid

Propylarsonic acid was reduced, on a 1.5 mmol scale, at 0 °C and, since the system was soluble in water, it was chromatographed [silica gel (13 g) in acetone; elution with acetone (90 ml) and methanol (70 ml)]. Some product eluted with acetone, together with dehydroascorbic and ascorbic acids. The product, which was eluted with methanol, was freed from silica-gel fines by take-up in chloroform (4 ml) and centrifuging. It was an oil (104 mg, 51%) soluble in $CHCl_3$, Me_2CO and MeOH. Found: C 22.23, H 5.23%. Calcd for C_3H_7AsO: C 26.89, H 5.27%; calcd for $C_3H_7As(OH)_2$: C 23.70, H 5.97%. The propylarsonic acid $C_3H_7AsO_3H_2$ requires C 21.43, H 5.40%. The product may contain traces of silica-gel fines. By NMR some —As—OH is present (see Eqn 2 below). IR (neat) (cm^{-1}): 2980 vs, 2872 vs, 2712 ms broad, 1462 m, 1406 w, 1380 w, 1200 w, 1078 w, 1044 w, 946 m, 900 m, 888 m, 828 (sh), 776 vs, 756 (sh), 720 s, 661 m. ^{1}H NMR ($CDCl_3$), δ: 1.04 (t, $J = 7.2$ Hz) and 1.11 (t, $J = 7.2$ Hz) for C*H*$_3$; 1.27 (s, 0.42H, ?); 1.65 (t, $J = 7.2$ Hz) and 2.36 (s) for C*H*$_2$As; 1.87 (d, $J = 7.2$ Hz) for C*H*$_2$; 6.54 (broad s, 1H, AsO*H*).

Allylarsonic acid

This was reduced, as in the case of propylarsonic acid. No arsenic(III) oxide was produced during the reduction. Evaporation and drying gave a white foam. Since the product was soluble in water, it was purified by column chromatography (silica gel, 10 g $mmol^{-1}$). Some product, together with ascorbic and dehydroascorbic acids, was eluted with acetone (90 ml $mmol^{-1}$) and the rest with methanol (70 ml $mmol^{-1}$). The yellow solid was taken up in chloroform and freed from brownish and white solid impurities. The yellow chloroform solution, upon evaporation and drying *in vacuo*, gave an orange semi-solid (38%) which on storage at −20 °C for a few days became dark brown and had higher contents (%) than expected of C and H. *Note*: the product was unstable.) The orange product had the following IR and NMR spectra. IR (neat) (cm^{-1}): 3082 w, 2972 w, 2918 w, 1756 w, 1674 w, 1634 m, 1422 w, 1396 w, 1190 w, 1050 w, 992 m, 918 vs, 888 vs, 826 s, 752 vs, 556 m. ^{1}H NMR ($CDCl_3$), δ: 1.27 (m, 0.23H, ?), 3.04 (t, $J = 7.2$ Hz, 2H, C*H*$_2$As), 5.34 (quartet, 2H, C*H*$_2$), 5.80 (br. s, 1H, AsO*H*), 5.89 (m, 1H, C*H*).

Benzylarsonic acid

This was reduced as in the case of propylarsonic acid. No arsenic(III) oxide was precipitated during the reduction. Evaporation and drying gave a white foam with a faint smell of bitter-almond (benzaldehyde).

Isolation by water extraction

The solid was dissolved in chloroform (15 ml $mmol^{-1}$) and extracted with water (4×4 ml). Some product was extracted into water as well. The chloroform phase was dried (Na_2SO_4), filtered and evaporated to give a white semi-solid with a faint smell of benzaldehyde. This was extracted with petroleum ether. The extracts contained three compounds (by TLC), two of which, benzyl alcohol (major) and benzaldehyde (minor), were verified by ^{1}H NMR. The residue, upon addition of chloroform, deposited, arsenic(III) oxide in an amount which increased with time. The IR spectrum had an additional peak at 884 cm^{-1} compared with that of the product isolated by column chromatography.

Isolation by column chromatography

Column chromatography of the reduced system (1 mmol scale) using 13 g silica gel in acetone, removal of ascorbic and dehydroascorbic acids plus some of the product and traces of benzyl alcohol with 150 ml acetone eluent and elution with methanol (70 ml), gave the product (260 mg) contaminated with silica-gel fines. These were removed by dissolving in chloroform (4 ml) and centrifuging. The product (250 mg, 69%) was a very viscous, colourless oil, contaminated by traces of benzaldehyde (by IR). The product was unstable in $CDCl_3$ (arsenic(III) oxide was deposited). The presence of arsenic(III) oxide, in the oil could not be detected by IR at 802 cm^{-1}. IR (neat) (cm^{-1}): 3082 w, 3060 w, 3026 w, 2970 w, 2914 w, 1700 w, 1600 m, 1494 m, 1452 m, 1406 w, 1212 w, 1032 w, 904 w, 814 (sh), 756 vs, 745 vs, 696 vs, 666 m, 619 w. ^{1}H NMR ($CDCl_3$), δ: 1.17 (d, ?), 3.50 (s, C*H*$_2$As), 4.63 (s, PhC*H*$_2$OH), 6.32 (broad s, AsO*H*, PhCH$_2$O*H*), 7.20 (m, C$_6$*H*$_5$ and C*H*Cl$_3$), 10.04 (s, PhC*H*=O).

RESULTS AND DISCUSSION

Non-catalysed reductions

Hydroquinone or arsorbic acid (in MeOH at RT) and triphenylphosphine[24,25] (under various conditions) did not reduce allylarsonic acid.

Triethyl phosphite, which is a better deoxygenation agent than triphenylphosphine[26] (in toluene at 85 °C) mostly decomposed ally- and benzylarsonic acids but not phenylarsonic acid, to arsenic(III) oxide. The mechanism of the decomposition involves attack of the phosphite at the α-carbon (and/or at the γ-carbon of allylarsonic acid) to give $R—\overset{+}{P}(OEt)_3$ which is attacked by the $^{-}O—As(OH)_2$ to give the Arbuzov product, $RPO(OEt)_2$, and $EtO—As(OH)_2$, which decomposes to As_2O_3, EtOH and H_2O. When, excess phosphite is used, the $R—\overset{+}{P}(OEt)_3$ is now dealkylated by $P(OEt)_3$ to the Arbuzov product and to the new phosphonium salt, $Et—\overset{+}{P}(OEt)_3$. This is now dealkylated by the very weak[27] nucleophile $^{-}O—As(OH)_2$ to give $Et—PO(OEt)_2$ and $EtO—As(OH)_2$. The latter decomposes as above.

Sodium cyanoborohydride did not reduce phenylarsonic acid (either alone or acidified) in methanol, but gave salts of $PhAsO_3H^{-}$, having the characteristic peaks for a monoanion in the IR,[23] with boron species containing HO—B—CN or H—B—CN groups.[22]

Iodide-catalysed reductions

The methanol-soluble tetrabutylammonium iodide did not reduce allylarsonic acid without an H^{+} source. Acidification with H_2SO_4 produced Bu_4NI_3 and 20–50% C–As bond fission, depending on the amount of H_2SO_4 present. The system $2Bu_4NI + H_2SO_4$ is essentially that of Irgolic *et al.*[7] for the preparation of diiodoarsines, $R—AsI_2$.

Hydroquinone in methanol did not reduce allylarsonic acid in the presence of 3 mol% iodine.

Boiling aqueous formic acid in the presence of iodine, as catalyst, had no effect on phenylarsonic acid but decomposed allyl- and benzylarsonic acids. A stoichiometric amount of oxalic acid in boiling water likewise resulted in decomposition of allyl- (15%) and benzylarsonic (74%) acids after 3 h. In these cases, the overall reaction is likely to be as represented by Eqn [1], and will proceed by attack of the 1^{-} at the α- (or γ-) carbon to give arsenic(III) oxide (via H_3AsO_3) and RI, which is hydrolysed to ROH and HI. The latter starts a new cycle by attacking the carbon atom.

$$2\,RAsO_3H_2 \xrightarrow[H_2O,\ reflux,\ I_2]{HCOOH\ or\ (COOH)_2} 2\,ROH + As_2O_3 + H_2O \qquad [1]$$

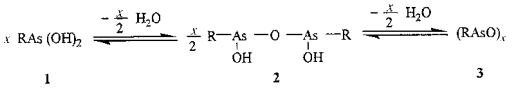
Acsorbic acid plus 3 mol% iodine (I_2) did not reduce allylarsonic acid in de-aerated water (RT/19 h). With 6 mol% I_2, some arsenic(III) oxide, (by IR) was produced after 24 h at RT, and the overall reaction must be as in. Eqn [1]. However, ascorbic acid and 3 mol% I_2 in de-aerated AR *methanol* (which contained traces of water) reduced allyl- and benzylarsonic acids in less than 10 min. Excess of ascorbic acid did not reduce the arsonic acids beyond the arsenoso stage because the excess was always seen on the thin-layer chromatograms. The reason why reduction takes place in methanol and not in water is given later.

Trialkyl phosphites plus 3 mol% I_2 in methanol at 0 °C reacted partially with allylarsonic acid to give 6–40% decomposition and some arsenoso compound. The system is quite complicated and formation of unreactive species, like $(RO)_2POI$/$(RO)_2P(O)OMe$, can explain the presence of unreacted arsonic acid. Likewise, triphenyl phosphite plus 3 mol% I_2 (MeOH/RT/7 h) decomposed 40% of the allylarsonic acid while 30% of the acid was recovered. The incomplete reaction may be attributed to the production[28,29] of species, such as $(PhO)_4P^{+}I^{-}$ and $(PhO)_2PI$, which are inactive towards the arsonic acid.

Triphenylphosphine reacts with I_2 to give Ph_3PI_2.[30] This adduct reduced sulphoxides in refluxing MeCN[31] and arenesulphonic acids in refluxing benzene.[32] We found that stoichiometric amounts of triphenylphosphine in the presence of 3–6 mol% I_2 quickly reduced arsonic acids at RT or 0 °C.

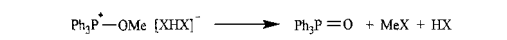
The solvent and temperature affected the reduction of allylarsonic acid by Ph_3P/I_2. In toluene the arsonic acid was insoluble and its reduction was incomplete after three days at RT. In dichloromethane the acid was insoluble, but after one day at RT 80% decomposition took place. In DMF or in MeOH/glyme, in which all the reactants were soluble, the exothermic reaction gave 60% decomposition after 10 min at RT. In pyridine, in which all the reactants were soluble, the reaction, after 17 h at RT, was incomplete and 70% decomposition was found. In water, in which Ph_3P was insoluble, the solution took 10 days to clear and much $Ph_3P^{+}—CH_2CH{=}CH_2$ plus H_3AsO_3 were seen on TLC. In methanol, in which Ph_3P was sparingly soluble, the exothermic reaction was over in 2 min

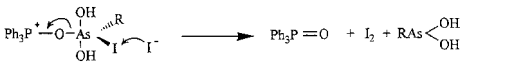
but 40% decomposition was found. At 0 °C no arsenic(III) oxide was produced with 3 mol% I_2, but 10% C–As bond fission occurred with 6 mol% I_2. In all reductions, traces of a salt of Ph_3P^+—R (even Ph_4P^+ with phenylarsonic acid) were detected by TLC. Traces of water in methanol and the water produced from the reactions in Eqn [2] did not deactivate the Ph_3P/I_2 system, as was observed in other reductions,[32] because hydrolysis of Ph_3PI_2 gives HI which can reduce the arsonic acid.


[2]

Hexamethylphosphorous triamide reduced arsonic acids in the presence of iodine in de-aerated methanol or chloroform at as low a temperature as the arsonic acid allowed. A salt of $(Me_2N)_3P^+$—R was detected by TLC, even when the amide was added very slowly.

The mechanism of the reduction of arsonic acids by Ph_3P, or $(Me_2N)_3P$, and I_2 involves the formation of the phosphonium salt Ph_3P^+—I·I^-. This, then, attacks the As=O or As—OH group in non-protic solvents, or instantaneously reacts with methanol[33] to give Ph_3P^+—OMe·$[IHI]^-$, or with water to give Ph_3PO and HI. Since the reaction (Eqn [3]) is slow,[33–35] it does not take place in our system (otherwise the reduction would have not taken place because I_2 is in catalytic quantity). Instead, the $Ph_3\overset{+}{P}$—OMe attacks the —As=O to give the 'protonated' intermediate, which is probably in equilibrium with the two P(V)–As(V) species (Scheme 1). From these, reduction to arsonous acid takes place *via* the alkyldihydroxydiiodoarsorane[7] (Scheme 1) or *via* attack by I^- at the As–I (Eqn [4]).[31,32]

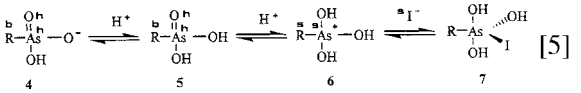

[3]


[4]

Since Ph_3P in the absence of I_2, does not react with arsonic acids, the C–As bond breaking must result from attack by another Ph_3P molecule at the α-carbon (and/or γ-carbon in the case of allylarsonic acid) of the intermediate, giving arsenic(III) oxide and $Ph_3\overset{+}{P}$—R(Scheme 1). Methanol, H_2O or I^- does not attack the α-carbon since we did not detect (by TLC) the corresponding compounds in the reductions of *rac*-2,3-dihydroxypropylarsonic acid.

Arsenic acid is reduced by I^- in 4 M aqueous HCl,[21b] and arsonic acids are reduced by SO_2/I_2 in concentrated aqueous hydrohalic acids[6] and by HI in aqueous or organic solvents.[7] These facts, as well as our results, point towards the notion that protonation of the $—AsO_3H_2$ group is required *before* I^- can act as a reducing agent, and can be understood by the 'hard and soft acids and bases' (HSAB) concept.[36,37]

In the sequence in Eqn [5], in going from **4** to **6** the arsenic becomes softer. In particular,[37] protonation (**5**→**6**) creates a vacant orbital on arsenic ready to accept the soft nucleophile, I^-. The equivalent of protonation can also be achieved by $Ph_3\overset{+}{P}$—OMe.

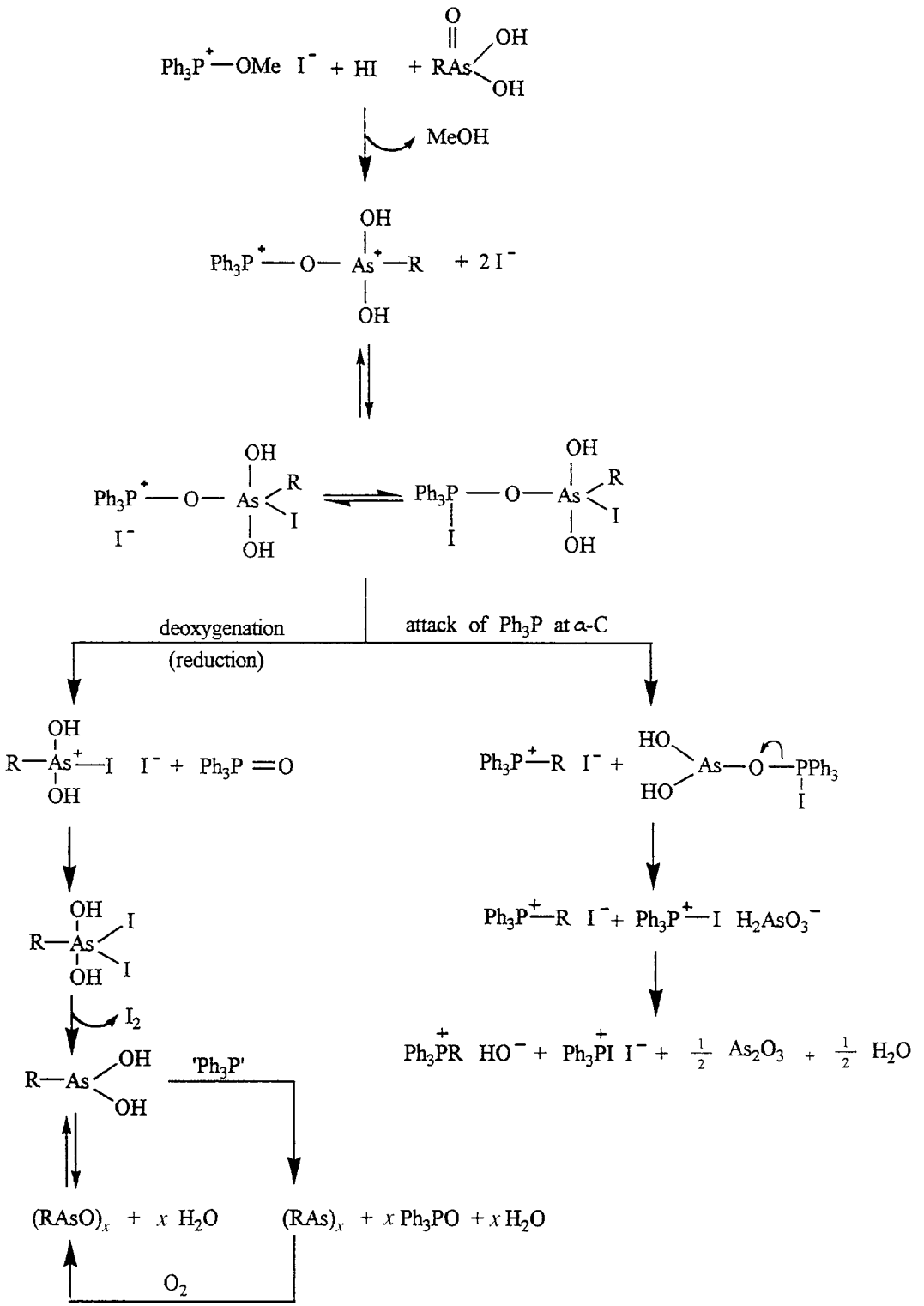

[5]

Triphenylphosphine is a soft base and in the *un*catalysed reaction should attack the borderline acid carbon in **5**. Since no reaction was observed, it seems that it does not have appropriate softness. On the contrary, trialkyl or triaryl phosphites, being harder bases than phosphines,[37] attack at the borderline acid carbon of **5**.

Arsonic acids as a class are stronger acids than carboxylic acids, having $pK_a \simeq 4$ in water.[1a] The pK_a, in water, of formic acid is 3.68; oxalic acid has pK_a values of 1.25 and 4.24, and ascorbic acid 4.19 and 11.57.[38]

In water our arsonic acids should be ionized (**4**), and in the presence of HCOOH, $(COOH)_2$ or ascorbic acid, as auxiliary reducing agents, protonation to **6** probably does not take place to a sufficient extent. Then, the soft I^- attacks the borderline acid carbon, breaking the weaker C–As bonds. In water, the insoluble Ph_3P and I_2 give Ph_3PO and HI, and the ionized arsonic acid, **4**, is attacked by I^- to give RI which reacts with Ph_3P to give the observed Ph_3P^+—R · $H_2AsO_3^-$.

In methanol which is a weaker base than water,[39] arsonic acids should largely be un-ionized (**5**), and protonation by HI to give **6** in the ascorbic acid/iodine system does take place. Then the soft I^- prefers to attack the soft As to give **7** because it has *d*-orbitals to accommodate the electron pair of the I^- and because of the attraction of the opposite charges. With triphenylphosphine as an auxiliary reducing agent, 'protonation' is achieved by $Ph_3\overset{+}{P}$—OMe. Now, in the system there are two soft

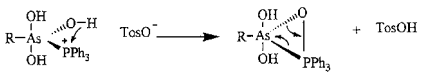


Scheme 1

acid sites and two soft bases (I^- and Ph_3P). The I^- prefers the positive arsenic in **6** (see above), leading to reduction. The Ph_3P attacks the soft α-carbon (a carbon next to a positive centre is soft[37]). This unwanted reaction can be depressed, but not totally avoided, by lowering the concentration of Ph_3P, e.g. by lowering the reaction temperature or by dropwise addition of a dilute solution of the reagent [Ph_3P or $(Me_2N)_3P$] at low temperatures.

Analogous arguments hold for the reactions of Ph_3P/I_2 run in non-polar organic solvents.

Protonated arsonic acids should be efficiently reduced by other soft bases, e.g. SCN^-, RS^-, R_3P and RSH, and less efficiently by borderline bases, e.g. Br^-. The $Ph_3P/(SCN)_2$ system gives $Ph_3P{=}S$ immediately[40]; the Ph_3P/PhSSPh system in methanol giving $Ph_3P{=}0$, PhSH and PhSMe,[41] was not tested for its reduction ability. Protonated by 20 mol% *p*-toluenesulphonic acid, allylarsonic acid in methanol consumes the Ph_3P in *ca* 6 h at RT. The mechanism of this reduction should involve the intermediates shown in Eqn [6]. Benzylarsonic acid in methanol reacts slowly with Ph_3P/Br_2 (TLC analysis).



[6]

The very fast reduction of arsonic acids with stoichiometric amounts of thiols to give $RAs(SR')_2$ and R′SSR′ in the *absence* of added acid,[10,11,13,42] and of *p*-amino-substituted phenylarsonic acids by phenylhydrazine,[8] can be rationalized in the HSAB framework assuming four-centred transition states.[37]

Finally, the puzzling reports on the reduction of alkylarsonic acids by SO_2/H_2O, mentioned in the introduction, may be explained by assuming that traces of I^- (from the less volatile alkyl iodides used for their preparation) contaminated the starting material. Similarly, the reduction of phenylarsonic acid by $NaHSO_3/H_2O$ was probably catalysed by I^- (or other soft bases) from the wooden tank used as a reaction vessel.

Preparation and isolation of arsenoso compounds by iodide-catalysed reductions

TLC is not a useful technique to detect the *complete* reduction of arsonic acids, because in MeOH or MeOH/conc. NH_3 (4:1) the product runs just above the arsonic acid. We therefore developed a sensitive test for detecting arsonic acid in the system: a drop of the solution is added to three drops of a saturated solution of lithium hydroxide in methanol. When arsonic acid is present, then a white precipitate of its dilithium salt is formed *at once*.

When equimolar quantities of arsonic acid and triphenylphosphine, in the presence of I_2 in methanol, were used, the reduction was not complete although all the triphenylphosphine had reacted. Control experiments (in the presence of hydroquinone) showed that triphenylphosphine did not react with dioxygen, in accordance with Buckler's findings,[43] but it probably reacted, as Ph_3PI_2 or Ph_3P^+—OMe·I^- with the arsonous acid, reducing it to the arseno compound, $(RAs)_x$. Since arseno compounds are quickly oxidized to arsenoso compounds by dioxygen, especially in the presence of I_2 or HI,[44] we could not detect it on TLC or in the final product. Therefore, for preparative purposes we used 50% excess triphenylphosphine. Under these conditions phenyl-, propyl- and *rac*-2,3-dihydroxypropylarsonic acids were reduced in 2–3 h at RT or 0 °C but allyl- and benzylarsonic acids decomposed (78 and 56%, respectively) during the reduction at 0 °C. All reactions produced traces to very small amounts of the corresponding Ph_3P^+—R. Separation of the product from the Ph_3P/Ph_3PO was effected by column chromatography. Acetone eluted the Ph_3P/Ph_3PO together with some product, probably in the form of $RAs(OH)_2$, and methanol eluted the product as $(RAsO)_x/RAs(OH)_2$, contaminated by a salt of Ph_3P^+—R. Phenylarsine oxide was obtained in 72–85%, arsenoso(*rac*-2,3-dihydroxypropane) in 77–85%, and arsenosopropane in 22%, yield. In the latter case most of the product eluted with acetone. Extraction of the hydrophilic arsenoso(*rac*-2,3-dihydroxypropane) by warm water from the Ph_3P/Ph_3PO was not an efficient process.

Polymer-bound triphenylphosphine[18] was tried in an attempt to separate the Ph_3PO from the $(RAsO)_x$ easily. Phenylarsonic acid gave 70–85% $(PhAsO)_x$, while 81% allylarsonic was recovered. These results can be explained by assuming that not all bound phosphine is accessible to alkylarsonic acids, whereas it is accessible to aromatic arsonic acids.

Another strategy to effect the separation of water-insoluble arsenoso compounds is to use hexamethylphosphorous triamide, which is oxidized to the water-soluble hexamethylphosphoric triamide (HMPA).[31b] But the mixture of arsenobenzene/HMPA was water-soluble and column chromatography in the case of HMPA/$(PhAsO)_x$ was not effective, for only a small amount of

HMPA was eluted with acetone, while most of it co-eluted with the product, probably because of the higher polarity of HMPA.

Ascorbic acid/iodine should be used in wet[17] deaerated methanol for the reduction of arsonic acids. The water produced from the reaction (Eqn [2]) also helps the reduction of I_2 by ascorbic acid. The dehydroascorbic acid which is produced is the hydrated (peak at 1700 cm^{-1} in the IR) and not the anhydrous[45] one. The anhydrous acid is insoluble in common organic solvents[45] whereas the hydrated acid is soluble. For preparative purposes, a 20–50% excess of ascorbic acid in the presence of 3–6 mol% I_2 was used. The end of the reaction was checked by the lithium hydroxide test (in this case, in a few minutes the test solutions turn yellow and then a yellow/orange mass is formed). In no case was arsenic(III) oxide formed during the reduction, but traces of benzaldehyde were formed when benzylarsonic acid was reduced. Isolation of the product can be effected by extracting the ascorbic/dehydroascorbic acids with water or half-saturated sodium hydrogencarbonate (for arsenosobenzene, but not for the other arsenoso compounds) or by chromatography, as in the case of Ph_3P/Ph_3PO. The yields were 70–90%.

Summarizing our results on the auxiliary reducing agent: triphenylphosphine should be the first choice, provided that the C–As bond is strong. Some functional groups are known to react with Ph_3P/X_2 systems (see Ref. 46 for a summary) but the reduction of the —AsO_3H_2 group being very fast should not pose a problem in reducing complex arsonic acids. An example is the reduction of *rac*-2,3-dihydroxypropylarsonic acid, where we did not detect —CH_2I, epoxide or alkene production. If some arsonic acid is reduced to the arseno compound, the latter is re-oxidized by air to the arsenoso compound during the work-up. The yields are very good, but the product is contaminated with traces of a salt of Ph_3P^+—R, an impurity which does not interfere in the Auger reaction[2] for the preparation of arsinic acids.[47] Ascorbic acid/iodine should become a valuable reducing system. It reduced the very labile allyl- and benzylarsonic acids without breaking the C–As bond, and the work-up can be very simple. The yields are acceptable to very good. In some cases the product was contaminated with traces of dehydroascorbic acid, which imparted a yellowish[45a] colouration to the product. The colour darkens to reddish or brown with storage. Hexamethylphosphorous triamide, being expensive and very easily oxidizable by air, should be used only in special cases.

The products are stable during storage except for the allyl and benzyl compounds. The decomposition of benzylarsonic acid during the reduction, to benzaldehyde and benzyl alcohol, and of the isolated arsenosotoluene to arsenic(III) oxide, cannot be explained. Benzaldehyde and arsenic(III) oxide were also the products of hydrolysis of benzyldichloroarsine.[48]

The melting point of an arsenoso compound $(RAsO)_x$ is not a safe indicator of its purity because it varies with the value of x. For example, the arsenosobenzene $(PhAsO)_x$ has the following melting points (as summarized by Steinkopf *et al.*[5]): 118–120, 129–130, 142–145 and 210–220 °C. The tetramer ($x = 4$) has m.p. 142–144 °C[44] and the polymeric ($x = ?$) has m.p. 210–220 °C.[5] Our arsenosobenzenes had m.p. 118–120 °C and, in a few cases, 128–129 °C.

In the ^1H NMR spectra of all aliphatic arsenoso compounds there is a sharp peak of variable intensity in the region $\delta = 1.15$–1.27 which we could not assign. In the spectra of propyl, allyl and benzyl arsenoso compounds in $CDCl_3$ there is one broad peak, and in that of arsenoso(*rac*-2,3-dihydroxypropane) in DMSO-d_6 (but not in D_2O) there are two strong and two weaker broad peaks in the region $\delta = 4.70$–7.80, indicative of —OH group(s) on arsenic, implying that these arsenoso compounds are in equilibrium with the other species of Eqn [2]. The ^1H NMR spectra of our aliphatic arsonic acids in D_2O show the $CH_2AsO_3H_2$ protons as one peak at specific δ values. Upon reduction these protons move upfield [consistently with the lower electronegativity of As(III) compared with As(V)] by 0.36 for allyl, 0.46 for benzyl, 0.50 and 1.20 for propyl, and 0.52 and 0.91 δ values for *rac*-2,3-dihydroxypropyl arsenoso compounds. For the latter two cases we are not certain whether the peaks should be attributed to different species of Eqn [2] or we are dealing with multi-spin systems. The same can be said for the —CH_3 and —CH_2OH (but not for the —CH_2- and —C*H*OH) protons of propyl and *rac*-2,3-dihydroxypropyl arsenoso compounds.

The IR spectra of aliphatic[49,50] and aromatic[49] arsonic acids and aromatic arsenoso compounds[8,51] have been discussed. The arseno compounds, lacking suitable groups,[8] cannot be detected by IR. The two strong peaks and a medium peak (or shoulder) at 922, 770, 820 cm^{-1} (propyl), 940, 772, 820 cm^{-1} (allyl), 900, 762, 820 cm^{-1} (*rac*-2,3-dihydroxypropyl), 892, 776, 820 cm^{-1} (benzyl) and 878, 776, 820 cm^{-1} (phenylarsonic acid), attributed to stretching vibrations of As═O and symmetric

plus asymmetric vibrations of As—O groups disappeared upon reduction. For $(PhAsO)_x$ we find two strong and sharp peaks at 742 and 722 cm^{-1} which are assigned[51] to asymmetrical and symmetrical As—O—As stretching vibrations. For the aliphatic products however, the shape of the strong peaks in the 780–720 cm^{-1} region differed. In the spectra of the propyl and allyl compounds a broad weak band at $\approx$2700 cm^{-1} is probably due to As—OH. The benzyl compound had a weak band at 3380 cm^{-1} due to benzyl alcohol, a very weak band at 2700 cm^{-1} due to As—OH and a weak band at 1700 cm^{-1} due to benzaldehyde and not to dehydroascorbic acid. The arsenic(III) oxide, if present in the oily benzyl arsenoso compound, could not be seen at 802 cm^{-1}.[20] Finally, in the spectrum of arsenoso(*rac*-2,3-dihydroxypropane) there is an extremely weak peak at 2712 cm^{-1}, due to As—OH, and five strong peaks at 1136, 1064, 1002, 954 and 626 cm^{-1} which we could not assign.

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